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<b>(21) International Application Number:</b> PCT/AU97/00264 <b>(22) International Filing Date:</b> 2 May 1997 (02.05.97) <b>(30) Priority Data:</b> PN 9606 2 May 1996 (02.05.96) AU <b>(71) Applicant (for all designated States except US):</b> COMMON-WEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Campbell, ACT 2601 (AU). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> Li, Sheng [CN/AU]; 6 Amott Court, Wheelers Hill, VIC 3150 (AU). GRIESSER, Hans, Jorg [AU/AU]; 20 View Road, The Patch, VIC 3792 (AU). <b>(74) Agent:</b> PHILLIPS ORMONDE & FITZPATRICK; 367 Collins Street, Melbourne, VIC 3000 (AU).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SURFACE MODIFICATION OF POLYMERS  <b>(57) Abstract</b>  A method of providing adhesion to a fluorinated polymer including exposing at least a portion of the surface of the fluorinated polymer to plasma discharge in an atmosphere containing an organic amine.		

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## SURFACE MODIFICATION OF POLYMERS

This invention relates to a method for improving the adhesion of materials to polymers including fluorinated polymers such as copolymers of ethylene and tetrafluoroethylene, and especially perfluorinated polymers such as the  
5 polytetrafluoroethylene (PTFE), perfluorinated ethylene-propylene polymers FEP, tetrafluoroethylene-ethylene copolymers (PFE-ET), hexafluoropropylene polymers (HFP) or fluorovinylether polymers also known as perfluoroalkoxy polymer (PFA).

### 10 Background to the Invention

Fluorinated polymers have a unique position in the plastics industry due to their chemical inertness, heat resistance, electrical insulation, low coefficient of friction and water repellancy. Notwithstanding the enormous advantages of fluorinated polymers their inert chemical nature, especially of perfluorinated  
15 polymers, makes them extremely hard to bond with adhesives. Fluoropolymers are not amenable to the usual surface modification techniques that have enabled adhesive bonding of hydrocarbon polymers. Surface treatments such as corona discharge and flame treatment, which are well known in the art for introducing bondable polar groups to the surface layers of, for example, polyolefins are  
20 ineffective with fluorinated polymers.

The presence of fluorine seems to markedly affect the chemical reactions occurring in polymer surface layers upon surface treatments. It is known that oxygen-containing or nitrogen-containing groups can be incorporated into the surface of, for instance, PTFE (Liston et al., *Journal of Adhesion Science and*  
25 *Technology*, 7, (1993)) and FEP (Xie et al., *Journal of Adhesion Science and Technology*, 6, 1411 (1993)) and the modified surfaces can be wetted, but adhesion is nevertheless poor. This poor adhesion has been attributed to a weak sub-surface structure of PTFE (Liston et al., *Journal of Adhesion Science and Technology*, 7, (1993)). Moreover the effects of ammonia plasma treatment are  
30 greatly reduced over a period of a few days due to surface layer motability (Xie et al).

The surface layers of perfluorinated polymers can be modified also by exposure to an etching solution that contains sodium naphthalene complex. PTFE surfaces etched thus can be adhesively bonded. The "sodium etch" method suffers, however, from considerable disadvantages. The high reactivity of the etch solution makes it dangerous to handle, requiring cumbersome precautions, and causes substantial disposal problems.

Attempts have been made to modify perfluorinated polymers by surface treatment methods such as corona discharge, flame treatment, and low pressure gas plasma (glow discharge) treatments, which pose far lower environmental hazards and are well established. The former two treatments are oxidative in nature and have not given satisfactory bond strengths. Low pressure plasma methods are more versatile in the choice of gas and enable introduction of various chemical groups onto polymer surfaces. However, in spite of many studies on, for instance, the introduction onto PTFE surfaces of amine groups to enable covalent adhesive bonding with cyanoacrylate or epoxy adhesives, no satisfactory process has been found; the bond strength was always found to be considerably below the cohesive strength of the material.

To improve subsequent adhesion perfluorinated polymers have been glow discharge treated in hydrogen/nitrogen mixtures (JP-A-6220231) (etching), in silane (JP-A-3164246), fluorocarbons or chlorfluorocarbons (DE-A-3408837) and in Ar, N<sub>2</sub>, O<sub>2</sub>, He or air (JP-A-3064382). Surface modification of PTFE by ammonia plasma treatment and its effect on bonding to nitrile rubber using a phenol-type adhesive was reported by Inagaki et al in J Adhesion Sci Technol Vol 3, no. 8, pp637-649 (1989). PTFE strips were given a ten minute treatment in a continuous 20kHz 150 mA plasma in 26Pa NH<sub>3</sub> atmosphere at various sample temperatures; only when the sample temperature reached over 200°C were bonds of strength exceeding the cohesive strength of the PTFE formed.

### Summary of Invention

We have discovered that the use of organic amine vapours in the plasma discharge treatment of fluorinated polymers offers significant improvements in the

adhesive bond strength compared with the ammonia plasma treatments described in the prior art.

Accordingly in one aspect the invention provides a method of providing adhesion to fluorinated polymers including exposing at least a portion of the surface of the fluorinated polymer to a plasma discharge in an atmosphere containing an organic amine. The surface of the fluorinated polymer may then be bonded to another material by contacting the surface with a suitable adhesive.

The organic amine used in the surface modification procedure may for example, be a hydrocarbyl amine comprising one or more amino group, a dihydrocarbyl amine or a polyhydrocarbylene polyamine.

When the organic amine is a hydrocarbyl amine or dihydrocarbyl amine the hydrocarbyl group may be branched, straight chain, cyclic-aliphatic or aromatic. Preferred hydrocarbyl are selected from the group consisting of alkyl, cycloalkyl, alkene and aryl. Aliphatic hydrocarbyl are more preferred.

The particularly preferred organic amines contain from one to twelve carbon atoms, more preferably from one to ten.

Specific examples of preferred hydrocarbyl amines and dihydrocarbylamines include methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, allylamine, 1,3-diaminopropane, diamino butane, cyclopentylamine, diisopropylamine, diaminocyclohexane and aniline.

Specific examples preferred polyhydrocarbylene polyamines include diethylenetriamine and triethylenetetramine.

Examples of adhesives which may be used in the process of the invention include cyanoacrylates, epoxy adhesives, structural acrylic adhesives, polyurethane adhesives, silicone adhesives, unsaturated polyester adhesives, contact adhesives or thermoplastic adhesives. The preferred adhesive chosen will depend on the nature of the material to be bonded to the polymer and the intended application of the assembly.

The method of this invention provides an effective pretreatment for achieving strong adhesive bonding. It has minimal environmental impact, and utilises equipment whose commercial use is established. We have found that the method of the invention typically allows an adhesive bond strength to be achieved

which is equal to the cohesive strength of the material. Furthermore unlike ammonia plasma treatment of fluoropolymer surfaces the present invention provides a long lasting improvement in bondability of the fluoropolymer surface. This provides an extended shelf life between treatment and bonding.

5           The invention also provides a fluoropolymer having an enhanced ability to bond to adhesives. Accordingly, in a further aspect the invention provides a fluorinated polymer the surface of which is bonded to a substrate with an adhesive and wherein the surface of the fluoropolymer has been treated with plasma discharge in the presence of an atmosphere containing an organic amine.

10           In another aspect the invention provides a composite comprising a first article having a surface of fluoropolymer which has been modified according to the above described method of the invention and a second article which has been bonded to the first article by an adhesive disposed between the second article and the modified fluoropolymer surface. The composite may contain two or more  
15 components and each may for example be formed of plastic which may optionally be reinforced, ceramic or metal.

          The fluoropolymer surface treated by the method may be a portion of the surface area. For example where only part of an article is to be bonded the plasma discharge may be localised to all or part of the area to be bonded. The  
20 fluoropolymer surface may be part of a film, foil, sheet or rod or can be in any other form such as a complex shape, component or composite.

          We have also found that the intermittent operation of the plasma discharge provides an unexpected advantage in increasing the adhesive bond strength when compared with corresponding treatments without intermittent operation.  
25           The invention therefore further provides a method for the treatment of a polymer surface, preferably a fluoropolymer or polyolefin surface, to increase the adhesive bonding strength thereto the method comprising exposing the surface to a vapour composition including at least one surface modifying agent and subjecting the surface to plasma discharge and wherein the polymer surface is subject to  
30 plasma discharge intermittently.

          The polymer surface may be intermittently subjected to plasma discharge in a number of ways. In one method the polymer being treated is stationary in a

plasma chamber in the appropriate atmosphere and the potential applied to the electrodes is cycled so that the plasma is alternately ignited and extinguished. In another method the polymer is repeatedly moved into and out of a single plasma discharge zone. Intermittent plasma treatment may also be achieved on a continuous production line by passing the polymer to be treated through a series of physically separated plasma discharge zones; in this case the ratio of plasma treatment time to no-discharge time is determined by the physical dimensions of the apparatus and the rate of transfer between discharge zones.

The polymer is typically intermittently subjected to plasma discharge with exposure periods of from 0.1 to 30 seconds. The time period between successive exposures is preferably in the range of from 0.1 seconds to 10 minutes. Typically the most preferred period between successive exposures to plasma discharge is from 0.1 to 30 seconds.

We have found that by using intermittent operation the bond strength for a given total plasma energy is significantly increased.

The benefits of intermittent plasma application are provided for a range of modifying vapours, and substrates. For example the vapour may be ammonia, water vapour, alcohols, amines or amides when the substrate is other than fluoropolymer.

The use of an intermittent discharge in modifying the surface of fluoropolymers using an organic amine vapour provides particularly good adhesion and can give rise to significant energy savings.

The improved bond strength provided by the process of the invention enables fluoropolymers to be more efficiently used in a range of applications. PTFE may be bonded as a facing to plastic or metal parts to take advantage of the low friction properties, the electrical insulating properties or resistance to corrosive chemicals.

The invention may use known low pressure plasma equipment modified to provide an atmosphere of the organic amine in the region of the plasma discharge.

The method of the invention may utilise additional components or steps. For example gases such as inert gases or organic ammonia may be used in

combination with the organic amine. Accordingly throughout the description and claims of this specification, the word "comprise" and variations of the word, such as "comprising" and "comprises", is not intended to exclude other additives or components or steps.

5           A suitable plasma discharge apparatus is shown in the drawings.

#### Brief Description of the Figures

Fig. 1 shows schematically a typical low pressure gas plasma setup suitable for the execution of the present invention.

10           The low pressure gas plasma set up of Fig. 1 is described in US 5,449,383 which is herein incorporated by reference.

Fig. 1 is a schematic view showing the parts of a plasma apparatus 3 for performing the process of this invention. A vacuum chamber 4 is evacuated by a pumping system 5 connected by an adjustable throttle valve 6 and an exhaust  
15   pipe 7. The pressure in the chamber is monitored by a pressure gauge 8. Vapour and gas streams are supplied to a mixing device 9 and reach the vacuum chamber 4 via an inlet pipe 10. Preferably, pressures of 0.1-1.0 torr are used.

Organic amine liquids are stored in thermostatted containers 11. Evaporation by boil off supplies organic amine vapour. Inorganic gases, such as  
20   ammonia and/or inert gases such as argon may be supplied from cylinders 12. All streams are individually controlled by flow control equipment 13 prior to reaching the mixing device 9. All streams may be used singly or in any combination.

High frequency electric power is provided by a source 14 via a matching  
25   network 15 to the electrodes 16. On application of electric power a discharge is established in the discharge zone 18 between the electrodes and as a result, the vapour becomes activated. From the gas plasma the activated products of organic amine or amines are polymerised as a thin layer 2 on to one or multiple surfaces of the bulk polymeric material 1.

30           Preferably the invention will utilise plasmas operating at frequencies of from 50 HZ to 100 GHZ at pressures of 0.01 to 10 Torr (more preferably 0.1 to 1



Torr). The total plasma power load per sample may be in the range of from  $10^{-4}$  W per  $\text{cm}^2$  to 1000 W per  $\text{cm}^2$ .

The invention will now be described in greater detail in conjunction with specific examples. It will be appreciated that the following examples are provided for the purposes of illustrating the invention and in no way should they be seen as limiting the scope of the above invention.

### Examples

In the following examples the surface of a range of substrates was treated by exposure to various plasma procedures and pairs of treated substrates bonded with cyanoacrylate adhesive. Tensile single-lap-shear tests were performed in dry condition according to ASTM D3165-73, except that lap shear coupons were of dimensions 50 x 25 x 3 mm (length x width x thickness) and the overlap was 25 x 3 mm. After bonding, the specimens were allowed to cure for 72 hours at room temperature in air prior to mechanical testing. Tests of bonded specimens were carried out on an Instron testing machine at room temperature in air  $21 \pm 2^\circ\text{C}$ ; relative humidity =  $50 \pm 5\%$ ), at a crosshead speed of 0.1 cm/min. A minimum of three specimens was tested in each case.

#### Example 1 - Effect of Plasma Gas

In this example the surface of PTFE coupons were modified by various plasmas in the plasma reactor illustrated in Figure 1. After plasma surface modification, the coupons were bonded with cyanoacrylate adhesive (LOCTITE 406). The treatment conditions and bond strengths are summarised in Table 1.

The surface modifications were:

- i) no treatment;
- ii) ammonia plasma treatment operated at 175kHz, 0.5 torr and 25 watts and at various duration;
- iii) plasma polymerisation of n-butylamine performed at 175kHz, 0.3 torr and at various energy levels and treatment durations;
- iv) plasma polymerisation of 1,3 diaminopropane (DAP) done at 175kHz, 0.3 torr, 20 watts and various treatment durations.

Table 1: Lap shear strength of PTFE modified by various plasmas

Test Number	Plasma Type	Dissipated Energy (Watts)	Duration (Seconds)	Lap Shear Strength (MPa)
1	no treatment			0.2±0.2
2	NH <sub>3</sub>	25	40	2.3±0.3
3	NH <sub>3</sub>	25	60	2.7±0.5
4	NH <sub>3</sub>	25	120	3.4±0.5
5	NH <sub>3</sub>	25	240	4.1±0.2
6	n-Butylamine	25	20	4.9±1.0
7	n-Butylamine	25	40	6.3±0.8
8	n-Butylamine	10	100	6.4±0.3
9	n-Butylamine	25	60	6.7±0.2
10	n-Butylamine	35	40	5.9±0.2
11	n-Butylamine	50	60	5.8±0.1
12	DAP	20	5	7.1±0.8
13	DAP	20	10	8.3±0.3
14	DAP	20	20	8.2±0.4

As can be seen from specimen 1 of Table 1, untreated PTFE has very poor bonding. Ammonia plasma treatment improves the bonding strength but lap shear strength at optimal conditions ranges around 3 to 4 MPa. These values have been documented in the paper by Liston et al referred to above and are claimed to be unsuitable for industrial applications in the article by Inagaki referred to above. Plasma deposition according to this invention with n-butylamine or 1,3-diamino propane improves significantly the adhesion properties of PTFE. Compared to ammonia plasma the lap shear strength obtained with n-butylamine plasma polymerisation is 50% greater and with 1,3 diaminopropane more than 100% greater.

#### Example 2 - Effect of Power Application Mode

This example shows the bonding properties of PTFE modified by plasma polymerisation of alkylamine using continuous or intermittent power mode. PTFE

coupons were surface modified by these plasmas then bonded with cyanoacrylate adhesive (LOCTITE 406). Lap shear test was performed according to the method described in Example 1. Results obtained on specimens tested are summarised in Table 2.

5 The surface modifications were:

- i) plasma polymerisation of n-butylamine under continuous mode at 175 kHz, 0.3 torr and different energy levels and treatment durations;
- ii) plasma polymerisation of n-butylamine under intermittent plasma mode at 175 kHz, 0.3 torr and different energy levels and treatment durations. For this  
10 plasma mode, plasma generator was turned on at operating pressure and then turned off at wanted treatment duration. The plasma chamber was pumped down to less than 0.05 torr then adjusted to the operating pressure. Another cycle of plasma polymerisation was carried out;
- iii) plasma polymerisation of 1,3 diamino propane under continuous mode at  
15 175kHz and 0.3 torr;
- iv) plasma polymerisation of 1,3 diaminopropane under intermittent plasma mode at 175kHz and 0.3 torr.

20 Table 2: Lap shear strength of PTFE modified by continuous or intermittent plasma polymerisation of n-butylamine and 1,3 diaminopropane.

Test No.	Monomer	Plasma Mode	Dissipated Energy (Watts)	Duration (cycle x time (sec))	Total duration (seconds)	Lap shear strength (MPa)
16	n-Butylamine	Continuous	10	1x100	100	6.4±0.3
17	n-Butylamine	Continuous	25	1x60	60	6.7±0.2
18	n-Butylamine	Continuous	35	1x40	40	5.9±0.2
19	n-Butylamine	Intermittent	10	5x25	125	9.9±0.4*
20	n-Butylamine	Intermittent	25	6x10	60	9.8±0.4*
21	n-Butylamine	Intermittent	35	5x10	50	10.8±0.8*
22	n-Butylamine	Intermittent	50	5x6	30	9.2±0.6*
23	n-Butylamine	Intermittent	70	4x8	32	9.2±0.3*
24	DAP	Continuous	20	1x20	20	8.2±0.4
25	DAP	Intermittent	20	3x4	12	9.0±0.4*

\* Failure occurred in the substrate.

As can be seen from this table, at similar total treatment duration significant improvement in adhesion is achieved when plasma polymerisation with alkylamine is carried out under intermittent rather than continuous mode. The lap shear strength of PTFE modified by intermittent plasma of both n-butylamine and 1,3 diaminopropane exceeds 9 Mpa leading to deformation and cohesive failure of the fluoropolymer substrate.

### Example 3

This example illustrates the application of intermittent plasma polymerisation of alkylamine on other type of polymers. High density polyethylene (HDPE) and polypropylene (PP) were subjected to surface modifications with n-butylamine plasma polymer obtained under continuous or intermittent plasma mode and bonded with cyanoacrylate adhesive (LOCTITE 406). The lap shear strength of specimens tested is summarised in Table 3.

The surface modifications were:

- i) no treatment
- ii) plasma polymerisation of n-butylamine under continuous mode at 175kHz, 0.3 torr and dissipated energy of 25 watts;
- iii) plasma polymerisation of n-butylamine under intermittent plasma mode at 175kHz, 0.3 torr and dissipated energy of 25 watts.

Table 3: Lap shear strength of high density polyethylene and polypropylene surface modified by n-butylamine plasma polymerisation performed under continuous or Intermittent plasma mode.

T st No.	Substrate	Plasma Mode	Duration (cycle x time, seconds)	Total duration (seconds)	Lap shear strength (MPa)
26	HDPE	no treatment			0.5±0.3
27	HDPE	Continuous	1x60	60	10.9±0.5
28	HDPE	Intermittent	3x20	60	19.5±0.6*
29	HDPE	Intermittent	6x10	60	19.7±0.6*
30	PP	no treatment			0.5±0.3
31	PP	Continuous	1x60	60	7.0±1.4
32	PP	Intermittent	3x20	60	12.0±1.1
33	PP	Intermittent	5x10	50	18.2±0.3*

\* Failure occurred in the substrate

5

It can be seen from Table 3, although significant improvement of bonding strength is achieved by surface modification of continuous plasma polymerisation of n-butylamine, the adhesion performance is better when the plasma is operated intermittently at similar conditions. Failure occurred within the polymer substrates

10 for specimens modified under intermittent plasma.

#### Example 4

This example compares the bonding performance of PTFE surface treated by ammonia plasma under continuous mode or the Intermittent plasma. PTFE coupons were treated by ammonia plasma and bonded with cyanoacrylate adhesiv (LOCTITE 406). The lap shear strength of bonded specimens is reported in Table 4.

15

The surface treatments were:

- i) ammonia plasma treatment operated under continuous mode at 175kHz, 0.5 torr and dissipated energy of 25 watts;
- ii) ammonia plasma treatment operated under intermittent mode at 175kHz, 0.5 torr and dissipated energy of 25 watts.

Table 4: Lap shear strength of PTFE surface treated by ammonia plasma under continuous or Intermittent plasma mode and bonded with cyanoacrylate adhesive

Specimen No.	Plasma Mode	Duration (cycle x time, seconds)	Total duration (seconds)	Lap Shear Strength (MPa)
34	Continuous	1x20	20	2.1±0.6
35	Intermittent	2x10	20	4.5±0.5
36	Continuous	1x40	40	2.3±0.3*
37	Intermittent	4x10	40	4.5±1.0*
38	Continuous	1x60	60	2.7±0.5
39	Intermittent	6x10	60	4.4±0.8

From Table 4, it can be seen ammonia plasma treatment operated in intermittent mode provides better bonding strength than continuous mode. Lap shear strength is higher both at similar operating conditions and at optimal conditions for intermittent plasma treatment.

#### Example 5

This example demonstrates the bonding of PTFE modified according to the invention with epoxy adhesive. After exposure to butylamine plasma (n-butylamine plasma under intermittent plasma mode at 175kHz, 0.3 torr, 35 watts and other conditions specified in Table 5), PTFE coupons were bonded with an epoxy adhesive (Araldite 138). Untreated control coupons were also bonded using the same adhesive. The bonded specimens were subjected to the lap shear test according to the method described in Example 1. Results obtained on treated and untreated specimens are summarised in Table 5.

Table 5: Lap shear strength of PTFE modified by intermittent plasma polymerisation of n-butylamine

Test No.	Substrate	Plasma Mode	Duration (cycle x time, seconds)	Total duration (seconds)	Lap shear strength (MPa)
40	PTFE	no treatment			0.3±0.3
41	PTFE	n-butylamine	3x10	30	5.6±0.5

Finally, it is to be understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention as outlined herein.

CLAIMS

1. A method of providing adhesion to a fluorinated polymer including exposing at least a portion of the surface of the fluorinated polymer to plasma discharge in an atmosphere containing an organic amine.  
5
2. A method according to claim 1 wherein the organic amine comprises one or more compounds selected from the group consisting of hydrocarbyl amines comprising one or more amino groups, dihydrocarbyl amines and polyhydrocarbylene polyamines.  
10
3. A method according to claim 2 wherein in the hydrocarbyl amines and dihydrocarbyl amines the hydrocarbyl groups are independently selected from the group consisting of alkyl, cycloalkyl, alkene and aryl.  
15
4. A method according to claim 1 wherein the organic amines comprise from 1 to 10 carbon atoms.
5. A method according to claim 1 wherein the organic amine comprises one or more compounds selected from the group consisting of methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, cyclobutylamine, cyclopentylamine, allylamine, diisopropylamine, 1,3-diaminopropane, diamino-butane, diaminocyclohexane and aniline.  
20
6. A method according to claim 1 wherein the surface of the fluorinated polymer is contacted with an adhesive selected from the group consisting of cyanoacrylates, epoxy adhesive, acrylic adhesives, polyurethane adhesives, silicone adhesives, unsaturated polyester adhesives, contact adhesives and thermoplastic adhesives.  
25
7. A method according to claim 7 wherein the adhesive is a cyanoacrylate adhesive.  
30



8. A method according to claim 6 wherein the fluorinated polymer is a p rfluorinated polymer selected from the group consisting of polytetrafluoroethylene (PTFE), perfluorinated ethylene-propylene polymers (FEP), tetrafluoroethylene-ethylene copolymers, hexafluoropropyl ne polymers (HFP)  
5 and fluorovinylether polymers.
9. A method according to claim 8 wherein the perfluorinated polymer is PTFE.
10. An article comprising a surface of fluoropolymer wherein the fluoropolymer  
10 surface has been treated according to the method of any one of the previous claims.
11. A composite comprising a first article having a surface of fluoropolymer which has been modified according to the method of claim 1 and which further  
15 comprises a second article which has been bonded to the first article by an adhesive disposed between the second article and the modified fluoropolymer surface.
12. A method according to claim 1 wherein the surface of the fluorinated  
20 polymer is intermittently subjected to plasma discharge.
13. A method according to claim 12 wherein the fluoropolymer surface is intermittently subjected to periods of from 0.1 to 30 seconds of plasma discharge.
- 25 14. A method according to claim 12 wherein fluorinated polymer surface is repeatedly moved into and out of a plasma discharge zone.
15. A method according to claim 12 wherein the fluorinated polymer surface is passed through a series of spaced plasma discharge zones.
- 30 16. A method according to claim 1 wherein the plasma is operated at a frequ ncy of from 50 HZ to 100 GHZ and pressur s of 0.01 to 10 Torr.

17. A method of treatment of a polymer surface comprising exposing the surface of the polymer surface to plasma discharge in the presence of a vapour composition including at least one surface modifying agent wherein the plasma discharge is intermittently applied.

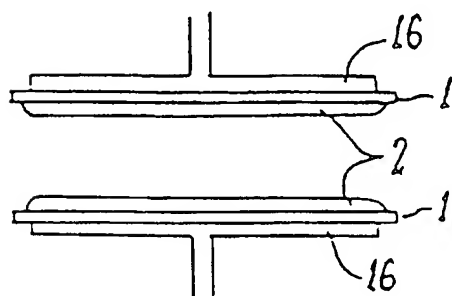
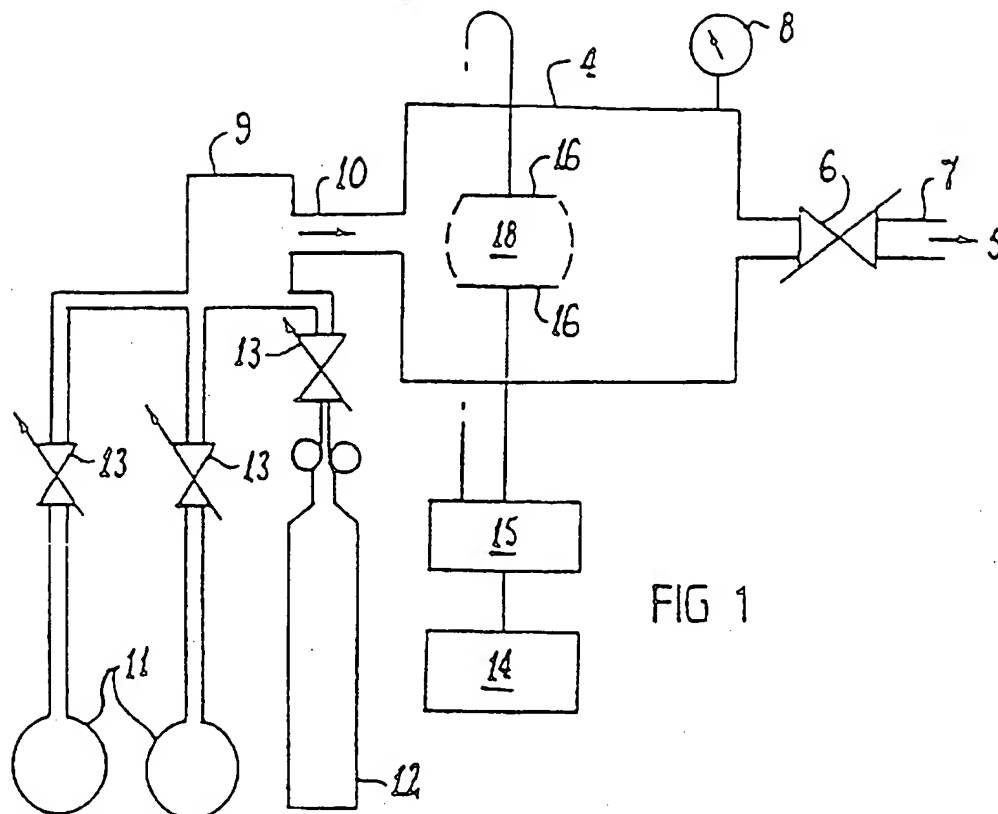


FIG 1a

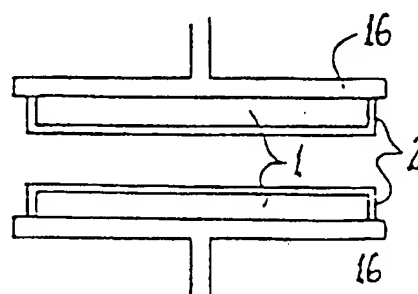


FIG 1b

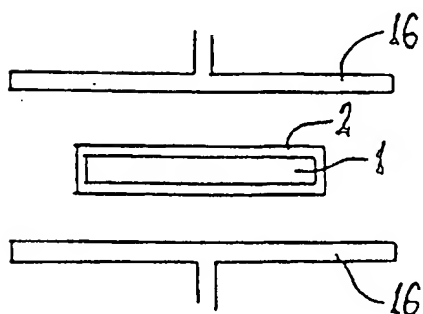


FIG 1c

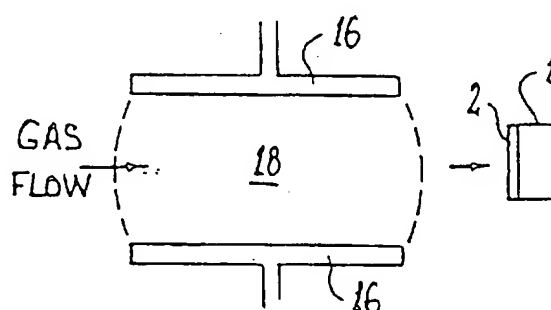


FIG 1d

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/AU 97/00264

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>				
Int Cl <sup>6</sup> : C08J 3/28				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols) IPC: C08J 3/28				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above.				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT: NITROGEN or N2 or Plasma JAPIO: NITROGEN or N2 or Plasma STN: NITROGEN (L) Plasma (L) [Teflon or PTFE]				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	Derwent WPAT Online Abstract Accession No.95-183065, JP, A, 07-102095 (NISSHIN ELECTRICAL CO. LTD) 18 April 1995 Abstract	17		
X	Derwent WPAT Online Abstract Accession No.96-371391, WO 96/23834 (SCHNEIDER USA INC.) 8 August 1996 Abstract	17		
<input type="checkbox"/> Further documents are listed in the continuation of Box C <span style="margin-left: 100px;"><input checked="" type="checkbox"/> See patent family annex</span>				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>			
Date of the actual completion of the international search 23 May 1997		Date of mailing of the international search report <b>02 JUN 1997</b>		
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (06) 285 3929		Authorized officer  <b>HUY PHAM</b> Telephone No.: (06) 283 2293		

### Information on patent family members

**PCT/AU 97/00264**

Patent Document Cited in Search Report	Patent Family Member
<b>JP      07-102095</b>	<b>NONE</b>
<b>WO      96/23834</b>	<b>AU      46983/96                  US      5532311</b>

END OF ANNEX